Radiation defects by Xe ion implantation and self-interstitial clusters evolution in molybdenum

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The formation of interstitial atom clusters in Mo lattice due to a high energy Xe+ ion bombardment was investigated using ab-initio and classical molecular dynamic simulations. By using a force-matching method, a new interatomic potential for pure Mo and a mixture of Mo and Xe atoms was developed. A defect self-organization after Xe bombardment was observed. Ab-initio calculations of formation energies of di-interstitials confirmed the general consequences of molecular dynamics. Defect clusters are readily formed at temperatures up to 2200 K. The more stable forms of clusters demonstrated 1D diffusion mechanism with very high diffusion coefficient. In the contrary, the vacancies have a diffusion coefficient of a few orders of magnitude lower than that of SIA clusters and do not evolve during the time of simulation.

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Radiation defects generated in various nuclear materials such as Mo, Fe and CeO2 as a surrogate material for UO2, formed by sub-MeV Xe and Kr ion implantations were actively studied in the last half century [1–6]. Although many features of the ion implantation have been explained, several phenomena are still not well understood: lattice swelling due to radiation [3, 7], formation of supperlattice of voids and bubbles [1, 4–6, 8] etc. More detailed information on the formation mechanisms and evolution of defects will be of critical significance in understanding of these problems. The previous studies were primarily related to properties of defect clusters in iron and copper [2, 9–12]. Molybdenum is a very important nuclear material since it forms several alloys with U demonstrating superior mechanical and thermophysical properties. However, it was not studied in detail by ab-initio previously. Self-interstitial atoms (SIA) were studied by quantum calculations in molybdenum [13, 14]. Although, the void superlattice formation in Mo is the most interesting and the oldest problem in the nuclear materials, it was not yet studied [1, 4–6].

In Refs [5, 15], Evans argued that the major reason for supperlattice formation in Mo is two-dimensional (2D) diffusion of SIACs in that material. To the contrary to these studies, other investigations [6, 8] predicted that one-dimensional (1D) diffusion of SIAs and clusters would play an important role in the supperlattice formation in Mo.

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The main subject of this article is a qualitative study of evolution of defects in pure Mo within a short time (about 1 ns) elapsed after cascade generated by an energetic Xe+ ion propagation. Specifically, we have studied the diffusion characteristics of the generic types of the self-interstitial atom clusters (SIAC) formed in cascade. These generic types of defects are of a fundamental significance related to the phenomenon of voids supperlattice formation.

Another goal of this paper is to develop a new many-body Xe-Mo interatomic potential and apply this new potential for studying radiation cascades in Mo.

By using molecular dynamic (MD) simulations, an evolution of Mo damage lattice was investigated after displacement cascades generated by a single Xe ion. Energy of a Xe ion was equal about 50 keV. It was assumed that there is no big difference between the cascades generated by an Xe-atom or Xe+-ion at such low energy kinetic energy. The charge of projectile have significance on first stage of interaction with sample surface which did not investigated in this work. Inside the Mo matrix, the Xe atom must relax to such state as well as Xe ion because of metal properties of environment (Mo matrix). As the first stage, we have developed a new interatomic potential for Mo-Xe systems by a force matching method (FMM) [16, 17]. The force − matching method provides a way to construct physically justified interatomic potentials even under such circumstances as absence of experimental data. The idea is to compute force and energies from first principles for a suitable selection of small reference systems and to adjust the parameters of the interatomic potential to optimally reproduce them.

Within the FMM, the reference data was calculated by a VASP ab-initio code [18]. The following main parameters of calculations of the reference data were used: the electron orbitals were represented using plane-waves, with a cut-off energy of 400 eV; the generalized gradient approximation (GGA) for pseudopotential; 8-points in k-space. 81 various configurations with total number of atoms equal 10746 were used in this calculation. These configurations presented a different Mo-Xe systems: 39 states with pure Mo (liquid and bcc. solid states at different densities; bcc. Mo with SIAs and/or vacancies and/or surface), 20 states with pure Xe (liquid and solid states) and 22 states with Mo-Xe (including a single Xe atoms in pure Mo). The matching was carried out with three types of values: energy (only one in every configuration); stress tensor (6 components in every configuration) and forces (fx, fy and fz per every atom in configurations). The calculated data was used in the FMM-procedures. The potential is realized in EAM (Embedding Atom Method) form for alloy with seven independent functions. In our

investigation the potential functions were set by splines with 10 independent parameters. The algorithm of search of potential parameters was implemented in the potfit-code [17] which was used in this work.

The developed interatomic potential [19] reproduces following data: the lattice parameters of Mo bcc lattice is equal 0.3147 nm; the experimental cold curves of pure Mo and pure Xe [20, 21] (up to pressure equal 700 GPa) and Mo thermal expansion at zero pressure [22] (up to melting temperature) reproduce with precision about 1-2 percent; melting line of Mo is like in work [23] (ab−initio calculation); equilibrium elastic constants of pure Mo reproduce to experimental data with precision about 20 percent; the experimental data on sputtering Mo by Xe ions [24] (dependence of sputtering yield on energy Xe ion) is simulated with good precision at Xe atom energy more than 50 eV. In addition the formation energies of SIAs and vacancy in pure Mo were calculated: crowdion — 6.42 eV; dumbbell <111> — 6.43 eV; dumbbell h110i — 6.67 eV; vacancy — 2.79 eV. The crowdion and dumbbell <111> are the more stable forms of SIA in Mo in accord with works [13, 14].

In MD-simulation the 1D-type of SIA diffusion was obtained having a diffusion coefficient equal to approximately 10−4 cm2/s. This value is of the same magnitude as the diffusion coefficient calculated for iron [2]. The 1D-diffusion mechanism is realized by jumps of SIA between the positions of a crowdion and a dumbbell <111> which both are located along the <111> axis. At thermal excitation of the dumbbell of the <110> type, the 1D-diffusion of a SIA can be superseded with a rotation in a (110) plane and therefore, the dumbbell pair can easily move along the other three equivalent <111> axis (which are the largest diagonals of the basic cube).

At temperatures higher than 1000 K, the 1D-type diffusion of SIA entirely transforms into a 3D-type of diffusion because of existence of big concentrations of dumbbell <110> types of SIA.

After the development and verification of the Xe-Mo potential, we carried out the simulations of radiation cascades in pure Mo by an Xe atom. The simulation box has the dimensions 9.4x9.4 x 94.4 nm3 with in 9.4 nm in the y and z directions and 94.4 nm along x-axis. A three dimensional periodic boundary conditions were used. Mo atoms formed bcc. crystal in the simulation box (at $5 < x < 94.4$ nm).

514392 atoms were used in these simulations. The ion irradiation direction was chosen to be were placed at 6° off normal to the top surface which was Mo (001) surface perpendicular to the ion irradiation direction. There are two crystal surfaces in the simulation box that were fixed during the whole simulation. These atom layers were modeled the rear surface of the film. Initial temperature of Mo lattice was set in the range of 50 — 2500 K.

All MD calculations were carried out by using a large-scale parallelized multipurpose MD code LAMMPS code developed at Sandia [25]. After preparation of the modeling system in an equilibrium state, one of the Xe atoms was placed above the top surface and a vertical component of the velocity was chosen according to the particle energy. The ion fluence was of about 1.1×10^{16} m^{-2}. Kinetic energy of Xe atom was equal 48.5 keV. The spreading Xe atom create track from disorder heated atoms of Mo and also create displacement subcascade from high energy atoms of Mo. We obtained that such Xe cascade produce about 100-130 SIAs and vacancies. However, the most of defect were recombined during first 1 - 2 ps of evolution time. Single vacancy have very small mobility with diffusion coefficient equal approximately 10−8 cm2/s and practically do not evolved during the time of simulation (but there is the recombination with SIA). Except the recombination of SIA and vacancy the main evolution process is the formation of SIACs. Characteristic states of Mo structure shown in figure 1. The SIAs formed clusters during evolution time equal approximately 0.5 - 1.0 ns.

Peculiar properties of this process:

— IAC is more stable formation than separate SIAs. Therefore at collision of two SIAs (or SIA and IAC) the fusion take place.

— More stable forms of IAC has 1D-type of thermal diffusion as well as SIA (with diffusion coefficient about 10−4 cm2/s like SIA). At minimal potential energy of IAC the crowdions are placed in parallel directions inside cluster (see figure 2 or type a of di-interstitial on figure 3).

This atoms arrangement is provided 1D-type of thermal diffusion. Some forms is similar to nanometer-sized dislocation loops. Note that 1D-diffusion of dislocation loop was obtained by experiment in iron [11].

— At temperatures below 800 K there is possibility of formation of stable immobile IAC (see on insertion a in figure 1). At high temperature the such immobile IACs is not formed. The existence of immobile defects cluster at low temperatures agree with results obtained for defect

cluster in iron [12]. This fact may be explained by existence of energy barrier between mobile and immobile

forms of IAC (type a and b respectively for di-interstitials on figure 3). Exclusive possibility of formation of immobile IAC at high temperatures is the collision two big mobile IAC.

—At increasing of IAC size the stability in relation the recombination with vacancy increase also. Big clusters may move near vacancies without change.

— The small share of defect get on surface of lattice. Therefore an some overbalance of vacancies arises.

— The clusters are formed up to temperature equal about 2200 K. At more higher temperatures the thermal fluctuations of potential energy prevent to formation of stable IACs.

For verification of simulation results, we performed the calculation of formation energy of di-interstitial by ab-initio method (with using of VASP code). In table the results of investigations are shown. Basic type of di-interstitials are shown on figure 3. Comparison of results of energy minimize by ab-initio and MD-simulation with new potential were carry out. The potential reproduce a defect hierarchy and energy with good precision. In figure 4 the dependencies of number of various IAC on evolution time are shown. At low temperatures there is approximately equal possibilities the formation of mobile or immobile IAC from SIAs. At temperature higher than 800 K an overbalance of mobile cluster was obtained. Note that the immobile IACs must have bigger lifetime than the mobile IACs because of the mobile cluster finally reach to surface and recombine (however time of this process exceed the simulation time on several orders).

The given work provides an opportunity to reconstruct the defect evolution on short time after the displacement cascade. At lower temperatures the immobile IAC is formed along with mobile IAC equally. There is large difference between this two type of IAC: mobile clusters are stable forms with 1D-diffusion mechanism whereas immobile clusters are unstable forms without diffusion.

The thermal fluctuations of atoms coordinates (accountable to the diffusion) inside the immobile IAC primarily lead to relax in the mobile form. The exception is possible only for very

big immobile IAC but it must have very slow diffusion (lower than vacancy). At high temperatures (800 K - 2200 K)the immobile IACs practically are dot formed and big mobile IAC are dominated during the evolution. At temperatures higher than 2200 K only the SIAs are observed. This objects fast recombine with the surface and vacancies.

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